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Amylopectin grafted with poly (acrylic acid): Development and application of a high performance flocculant

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ABSTRACT

In recent years, wastewater treatment, especially for wastewaters which are not suitably recycled by conventional or normal biological processes, is getting more importance. Of late, natural biopolymer based flocculants are extensively used for wastewater treatment because of low cost, environment-friendly and easily availablility from reproducible farm and forest resources. This article introduces the development of a natural polymer based flocculant [amylopectin grafted with poly (acrylic acid) – AP-g-PAA] for treatment of synthetic effluent as well as mining industry wastewater. The graft copolymer based flocculants have been developed under optimum conditions and characterized using viscometry, ^{13}C NMR, SEM, TGA, rheological characteristics, determination of hydrodynamic radius and CHN analysis. The flocculation characteristics of grafted and ungrafted polysaccharide have been evaluated in synthetic effluents (as Fe-ore, kaolin, Mn ore suspensions) as well as in mining industry wastewater.

1. Introduction

Industrial development and growing population lead to creating a paramount problem in potable water. To protect the environment and aquatic bodies from oblivious disposal of wastewater, it is essential to treat wastewater and its possible reuse. Untreated wastewater not only increases paucity of potable water but also it increases suspended solids, dissolved solids, turbidity and colouration of water, which retards photosynthesis, inhibit the growth of aquatic biota, and interferes with gas solubility in water (Deblonde, Cossu-Leguille, & Hartemann, 2011; Schwarzenbach et al., 2006). Exudation of wastewater from various industries contain finely divided particulate matter, with a diameter of 0.001–10 μm, which will not settle down of suspension by gravity because of very small size and surface charge (Brostow, Pal, & Singh, 2007). The removal of these colloidal particles from various wastewaters is becoming a challenging job.

Several technologies have been employed for the treatment of various wastewater and industrial effluents, out of which flocculation is an ecofriendly and economical process (Renault, Sancey, Badot, & Crini, 2009; Sharma, Dhuldhoya, & Merchant, 2006). It encounters most efficacious technique, in particular for removal of suspended particles, dyes, toxic heavy metals etc. (Crini, 2006). Flocculation is a process that destabilized the finely divided particles, accelerate to make large flocs, so as to be settled and separated from the wastewater (Chang, Hao, & Duan, 2008; Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011). Earlier, inorganic coagulants like alum, ferrous sulphate, poly $AlCl_3$, ferric chloride have been used for wastewater treatment. However, the major drawbacks of using inorganic coagulants are basically requirement of more quantity of coagulant for achieving an effective settling rate, resulting formation of huge sludges, which creates disposal problem (Joo et al., 2007). To overcome these problems, now-a-days, organic flocculants are used extensively due to their high tailorability, rapid settling and reduced sludge production. This minimizes the untoward effect of inorganic coagulants (Lee, Shin, Choi, & Park, 1998). Out of synthetic and natural organic flocculants, both are having some advantages as well as limitations. Synthetic polymers are highly efficient flocculant, however, they are not biodegradable and their degraded product is contemplated as a hazard because of release of toxic monomer which may cause serious threat to the environment (Schintu, Meloni, & Contu, 2000). On the other hand, natural polymer based flocculants have been acclaimed as "Green Flocculants of 21st Century" (Xiao & Zhou, 2005). They are shear resistant, biodegradable and eco friendly, but at the same time, less efficient as flocculant. In order to overcome these drawbacks of synthetic and natural polymer based flocculants, it is essential to combine the best characteristics of both synthetic and natural polymers. By grafting of synthetic polymers onto natural polysaccharide backbone, it is possible to combine the best properties of both. It has been observed that by grafting synthetic polymers onto natural polysaccharide backbone, it is possible to

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develop efficient flocculants with improved flocculation properties (Karmakar, Rath, Sastry, & Singh, 1998; Sen, Kumar, Ghosh, & Pal, 2009; Singh et al., 2000; Singh, Nayak, Biswal, Tripathy, & Banik, 2003; Tripathy & Singh, 2001). These graft copolymers are biodegradable as well as non-toxic in nature (Vijan, Kaity, Biswas, Issac, & Ghosh, 2012). Synthesis of graft copolymers essentially involves free radical mechanism. Out of several techniques, use of free radical initiator to generate free radical sites on polysaccharide as well as synthetic monomer is frequently used approach (Kang, Cai, & Liu, 2006; Singh, Pal, Krishnamoorthy, Adhikary, & Ali, 2009).

One of the most important natural polysaccharide is AP, which is a high molecular weight (between 50,000 and 10^7 g/mol) as well as highly branched polymer of α-D-glucopyranosyl residues linked together mainly by $1 \rightarrow 4$ linkages with $1 \rightarrow 6$ bonds at the branch points (Buleon, Colonna, Planchot, & Ball, 1998). On the other hand, PAA is an efficient flocculant for treatment of various wastewaters, as reported (Das & Somasundaran, 2001; Das & Somasundaran, 2003; Khalil & Aly, 2002; Mishra, Rani, & Sen, 2012; Yan, Glover, Jameson, & Biggs, 2004). Herein, we report the synthesis of a novel polymeric flocculant based on AP-g-PAA, its detailed characterization and application as efficient flocculant for the treatment of synthetic effluents as well as mining industry wastewater.

2. Experimental

2.1. Materials

AP was purchased from Fluka, Switzerland. Acrylic acid was procured from E. Merck Germany. Potassium persulphate was purchased from Qualigens, Mumbai, India. Analytical grade of acetone and hydroquinone were supplied by E. Merck Ltd., Mumbai, India. The chemicals were used as received without further purification. Kaolin was supplied by Jyoti Chemicals, Howrah, India. Iron ore, manganese ore was a gift sample from Tata Steel Co., Jamshedpur, India. Mining industry wastewater was collected from a mine near to Dhanbad, India.

2.2. Synthesis

2.2.1. Synthesis of graft copolymer (AP-g-PAA)

The graft copolymer of AP and PAA has been synthesized in inert atmosphere of nitrogen using potassium persulphate (KPS) as initiator. The typical synthetic procedure is as – 1 g of AP was slowly dissolved into 85 mL of distilled water in a three necked round bottom flask. The flask was fitted with an electrically operated magnetic stirrer (Tarsons, Model: Spinot Digital) and kept in an oil bath maintained at a temperature of $65 \pm 1\,^{\circ}C$, with constant stirring. Desired quantity of acrylic acid (Table 1) was mixed with the AP solution and continued to heat at the same temperature (65 °C), with constant stirring (450 rpm) for 30 min. At this stage, 5 mL of potassium persulphate solution of required concentration (Table 1) was added and the reaction was continued for another 1 h at same temperature and stirring speed. At the beginning, the reaction system was heterogeneous as acrylic acid is not well soluble in water and after adding KPS, the system becomes homogeneous. During the whole reaction, nitrogen gas was purged through reaction system. The reaction mixture was cooled to room temperature, washed with 200 mL of methanol–water solution (70:30) for removal of homopolymer (Xu, Wu, Huang, Cao, & Wang, 2006), if present. Afterwards, the resultant graft copolymer was precipitated by adding 250 mL of acetone so that unreacted monomer i.e. acrylic acid (if present) will be separated from the graft copolymer. Afterwards, the graft copolymer was dried in a hot air oven at 60 °C for 6 h, pulverized by mortar – pastel and sieved through a 125 μm sieve. The synthesis parameters are reported in Table 1.

2.3. Characterization

Intrinsic viscosity of AP and various graft copolymers were measured using Ubbelohde Viscometer in 1 (M) sodium nitrate solution. Hydrodynamic radius was measured by DLS analysis using Zeta-Sizer Nano-S 90 (Malvern, UK). C, H, N, O analysis was performed using an Elemental Analyzer (Model – VarioEL III, Manufactured by – M/s Elementar, Germany). ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in solid state (for AP and AP-g-PAA 5) and in liquid state (for acrylic acid; DMSO was used as solvent) at 500 MHz on a Bruker Advance II-500NMR spectrophotometer. Morphological characterization was carried out using scanning electron microscopy (Model: S-3400N; HITACHI, Japan). Thermogravimetric analysis of AP and AP-g-PAA5 was carried out with TGA instrument (Model: DTG-60; Shimadzu, Japan) – the study was performed up to 600 °C, starting from 25 °C, in an inert atmosphere (of nitrogen). The heating rate was uniform in all cases (5 °C/min).

2.4. Investigation of rheological characteristics

The rheological characteristics were conducted in the laboratory using Rheolab QC Rheometer (Model – C-LTD 180/QC; Anton Paar, Australia). The temperature of the system was maintained at 25 °C throughout the experiments. The aqueous solutions of AP (5 wt%) and all the graft copolymers (1 wt%) were prepared by adding required quantity of polymers slowly to distilled water with continuous stirring (300 rpm for 3 h) using a magnetic stirrer at a temperature of 60 °C.

2.5. Flocculation studies

2.5.1. Flocculation characteristics of graft copolymers using synthetic effluents (Fe-ore, Mn-ore and kaolin suspensions)

The flocculation efficiency of AP and various graft copolymers was carried out using settling test. To elucidate the flocculation mechanism, we have used three different types of suspensions (Fe-ore, Mn-ore and kaolin). The details of experimental procedure have been given in Supporting Information. The floc size was measured using DLS analysis (Zeta Sizer Nano-S90, Malvern, UK).

2.5.2. Flocculation characteristics of AP and various graft copolymers using mining industry wastewater.

The flocculation efficacy of AP and various graft copolymers was investigated for treatment of mining industry wastewater. The experiment was carried out in nine (9) different sets. 1st SET is the control set, where 200 mL of mining industry wastewater was treated without addition of any flocculant. Remaining 8 sets were consist of treatment of 200 mL of wastewater with 9 ppm of various flocculants i.e. AP and different graft copolymers. The details of experimental procedure as well as chemical analysis of treated and untreated wastewater have been given in Supporting Information.

3. Results and discussions

3.1. Synthesis

AP grafted with PAA was synthesized by free radical polymerization technique using KPS as free radical initiator, in inert atmosphere of nitrogen. By varying the reaction parameters, various grades of graft copolymers have been synthesized and reported in Table 1. The optimization of the best graft copolymer was determined through its highest % grafting efficiency (% GE), highest intrinsic viscosity and hydrodynamic radius values. The probable mechanism for formation of graft copolymer is based on the fact that, KPS generates free radical sites on the backbone of AP. These free radical sites then react with monomer (acrylic acid) to form

Table 1
Synthesis details of amylopectin grafted with polyacrylic acid.

Polymer	Initiator conc. (mol × 10^{-5})	Monomer conc. (mol)	% Grafting efficiency[a]	Intrinsic viscosity (dL/g)	Hydrodynamic radius (R_H) (nm)
AP-g-PAA 1	0.370	0.138	61.01	26.78	275.05
AP-g-PAA 2	0.925	0.138	62.31	33.95	507.50
AP-g-PAA 3	1.85	0.138	75.75	38.89	557.50
AP-g-PAA 4	2.77	0.138	72.10	30.27	334.70
AP-g-PAA 5	**1.85**	**0.173**	**86.57**	**47.27**	**628.00**
AP-g-PAA 6	1.85	0.208	64.52	38.75	526.50
AP-g-PAA 7	1.85	0.243	56.12	32.82	337.15
Amylopectin(AP)	–	–	–	1.38	139.75

[a] % Grafting efficiency $= \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of monomer}} \times 100$.
Bold values indicates that AP-g-PAA 5 graft copolymer is the optimized one & showed best performance.

graft copolymer through initiation, propagation and termination steps as shown in Scheme S1 (Supporting Information). Hydroquinone was used as inhibitor to stop the polymerization process.

3.1.1. Effect of initiator concentration

The effect of initiator concentration on % GE and intrinsic viscosity was investigated at constant temperature (65 °C), monomer and polysaccharide concentration (Fig. S1, Supporting Information). It has been observed that with increase in initiator concentration, % GE as well as intrinsic viscosity increased till 1.85×10^{-5} moles, beyond which it turns down. It is well known that a relatively low concentration of catalyst/initiator should initiate a few grafting sites (Nayak & Singh, 2001), which will result in longer grafted polymer chains [here it is PAA], compared to a high concentration of catalyst, which will initiate large number of grafting sites, making the average grafted polymer chains shorter for the same monomer concentration (Nayak & Singh, 2001). Hence, by grafting PAA chains onto AP, two possibilities are there (i) one can either have a small number of long PAA chains or (ii) a large number of short PAA chains in the graft copolymer. In the first case, the compact shape of the graft copolymer would be changed, because of the presence of longer grafted chains. This would result in larger hydrodynamic volume, leading to higher intrinsic viscosity (Table 1 as well as Fig. S1, Supporting Information). On the other hand, a large number of short PAA chains (i.e. second case) will not alter the original compact shape to a great extent and hence lower would be hydrodynamic volume (i.e. intrinsic viscosity) (Table 1 as well as Fig. S1, Supporting Information).

3.1.2. Effect of monomer concentration

Fig. S1, Supporting Information illustrates the influence of monomer concentration on % GE and intrinsic viscosity, having other reaction parameters (i.e. temperature, initiator concentration and polysaccharide concentration) constant. With increase in monomer concentration (from 0.138–0.173 mol), % GE enhanced continuously and achieved the maximum when the concentration of acrylic acid is 0.173 mol. Afterwards, % GE as well as intrinsic viscosity decreased. This may be because of the fact that an increase in monomer concentration leads to the accumulation of monomer molecules in close proximity to the polymer backbone. The decrease in the % GE as well as intrinsic viscosity after optimized concentration of monomer could be associated with the reduction in the active sites on the AP backbone as graft copolymerization proceeds. It is also assumed that with excess monomer concentration, the formation of homopolymer (which has been separated from graft copolymer by washing with methanol–water) will predominate, leading to diminution in % GE and intrinsic viscosity.

3.2. Characterization

3.2.1. Explanation of intrinsic viscosity, hydrodynamic radius

The intrinsic viscosities (Fig. S2, Supporting Information) of AP and various graft copolymers was measured in 1(M) $NaNO_3$ solution using Ubbelohdge viscometer and results are presented in Table 1. The intrinsic viscosity of all the graft copolymers is higher than that of base polysaccharide. This is because of the presence of grafted PAA chains onto the AP backbone. However, it is interesting to observe that the graft copolymer, which is having the highest % GE (i.e. AP-g-PAA 5), is having maximum viscosity. This indicates that the AP-g-PAA 5 contains longer PAA chains, which will increase the hydrodynamic volume of the polymer in solution i.e. intrinsic viscosity.

The hydrodynamic radius (R_H) of AP and graft copolymers were assessed using DLS analysis. It is obvious (Table 1) that R_H of graft copolymers is higher compared to that of AP, because of the presence of grafted PAA chains. Further, here also, AP-g-PAA 5, which is having maximum % GE is having maximum hydrodynamic radius.

3.2.2. Elemental analysis

The elemental analysis of AP and AP-g-PAA 5 shows (Table S1, Supporting Information) that there is a considerable amount of increase in oxygen content in the graft copolymer compared to AP. The increase in oxygen content in the graft copolymer is mainly because of the presence of grafted PAA chains onto AP backbone.

3.2.3. ^{13}C NMR spectroscopy

The ^{13}C NMR spectrum of AP (Fig. 1a) shows four distinct peaks at δ = 103.2, 82.3, 72.4 and 63.5 ppm, which can be attributed to the anomeric carbon atom, the carbon atom of $-CH_2OH$ group, carbon atoms connected by —OH groups in the six member ring except anomeric carbon atom (i.e. C-2 to C-4), and C-5 carbon atom, respectively. Acrylic acid (Fig. 1b) has three major peaks. The peak at δ = 170.4 ppm is due to carboxylic acid carbon. Peaks at δ = 127.5 and 132.2 ppm are for two sp^2 hybridized carbon atoms (i.e. $-CH{=}CH_2$). The solid state ^{13}C NMR spectrum of AP-g-PAA 5 (Fig. 1c) contains two additional peaks in compare with the ^{13}C NMR spectrum of AP. The additional peak at 172.5 ppm correlated to the carboxyl carbon, which is present in the spectrum of acrylic acid. Another additional peak at δ = 42.0 ppm can be accredited to sp^3 hybridized carbon atoms (i.e. $-CH_2-CH_2-$ groups), which is absent in the spectra of acrylic acid as well as AP. Interestingly, peaks at δ = 127.5 and 132.2 ppm, responsible for two sp^2 hybridized carbon atoms (i.e. $CH_2{=}CH-$) for acrylic acid, absent in the spectrum of AP-g-PAA 5. This indicates that sp^2 hybridized carbon atoms of acrylic acid monomers rehabilitated into sp^3 hybridized carbon atoms of PAA during polymerization and confirms that PAA chains have been grafted onto AP backbone through covalent attachment.

3.2.4. SEM analysis

Fig. 2, represents the scanning electron micrographs (magnification ×2.00 K) of (a) AP and (b) AP-g-PAA 5. A closure inspection of micrographs reveal that there is large difference in the morphological appearance of the native polysaccharide and the graft copolymer. AP has granular morphology. After grafting, the granular appearance of the native AP was distorted and transferred to

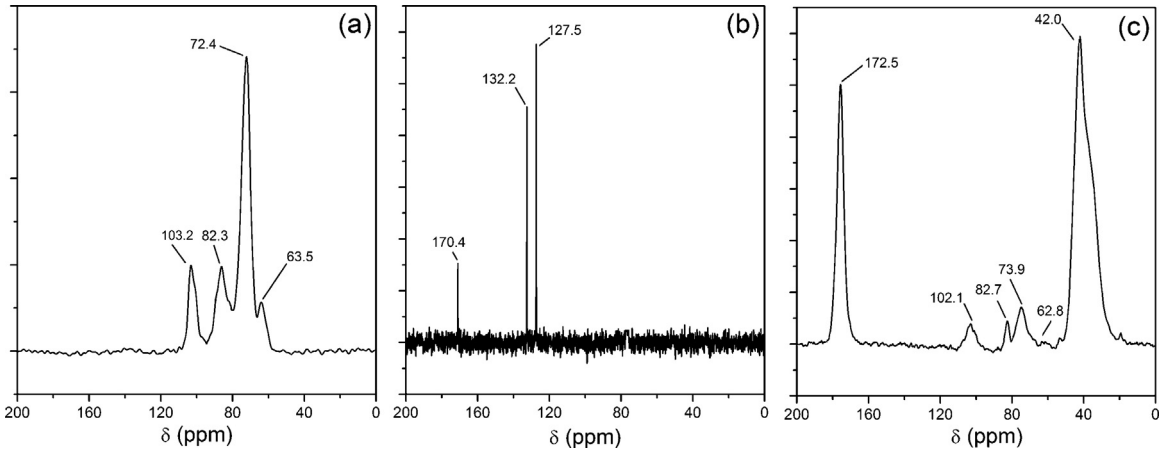

Fig. 1. ^{13}C NMR spectra of (a) AP, (b) acrylic acid, (c) and AP-g-PAA 5.

fibrillar morphology, as the grafted PAA chains got agglomerated. This observation implies that grafting of PAA affects the morphological characteristics of AP.

3.2.5. TGA analysis

The TGA curve of AP (Fig. 3a) basically involves two distinct zones of weight loss. The initial weight loss is in the temperature region of 25–100 °C, which is because of the traces of moisture present. The second zone of weight loss (280–350 °C) might be because of the degradation of the polysaccharide backbone. In case of AP-g-PAA 5 (Fig. 3b), the initial degradation zone is because of the presence of moisture. The second region of weight loss in the range of 200–280 °C, may be due to the degradation of polysaccharide backbone as well as decomposition of carboxyl group of grafted PAA chains (Chen, Wu, Liu, & Long, 2006; Garay, Alava, & Rodriguex, 2000). However, there is an additional zone of weight loss (i.e. 350–500 °C) in case of AP-g-PAA 5 in compare to AP, which is for the decomposition of the grafted polymer backbone (Chen et al., 2006; Garay et al., 2000). Therefore, the presence of this extra zone of weight loss is a clear indication that PAA chains have been grafted onto the backbone of AP.

3.3. Rheological characteristics

The rheological characteristics of AP and various graft copolymers notify that all the polymer solutions are pseudoplastic (Fig. S3 and Table S2, Supporting Information) in nature. AP-g-PAA 5 shows the highest shear viscosity followed by other graft copolymers and base polysaccharide at both high and low shear rate region. The higher shear viscosity of graft copolymers is because of the presence of synthetic PAA chains onto AP backbone. However, AP-g-PAA 5 is having highest shear viscosity, is because of maximum % GE i.e. the presence of longer PAA chains, which in turn will increase the viscosity of the solution. Another evidence is pseudoplasticity (n), calculated (Table S2, Supporting information) using the power law equation

$$\eta = K \cdot \gamma^{n} \tag{1}$$

where η is the apparent dynamic viscosity at a given temperature, n is flow behaviour index (less than 1 indicates pseudoplastic behaviour), K is consistency coefficient, a value that is proportional to the fluid's viscosity and γ is the shear rate. Intercept indicates zero shear viscosity which has direct proportionality to the gel microstructure. Slopes of best fitted straight lines indicate the rate of de-structuring on shearing. It is assumed that higher the slope, physically weaker is the gel as it loses its structure quite fast. Higher 'n' values for AP, all graft copolymers except AP-g-PAA 5 indicates faster de-structuring under shear while low 'n' values of AP-g-PAA 5 depicts slower rate of de-structuring under similar condition.

3.4. Flocculation characteristics

3.4.1. Flocculation properties in synthetic effluent

The flocculation characteristics of AP and various graft copolymers were explored in iron ore (Fig. 4a), kaolin (Fig. 4b) and manganese ore suspensions (Fig. 4c). As obvious, the settling profiles of the graft copolymers do not show any retarded settling behaviour. It is logical from the figure that in all the three suspensions, graft copolymers demonstrate better flocculation characteristics in compared with pure AP. This is because of the fact

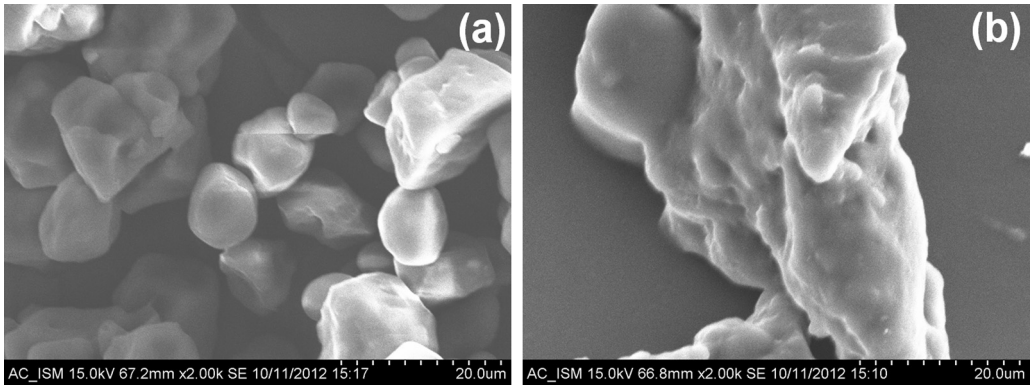

Fig. 2. Scanning electron micrographs of (a) AP and (b) AP-g-PAA 5.

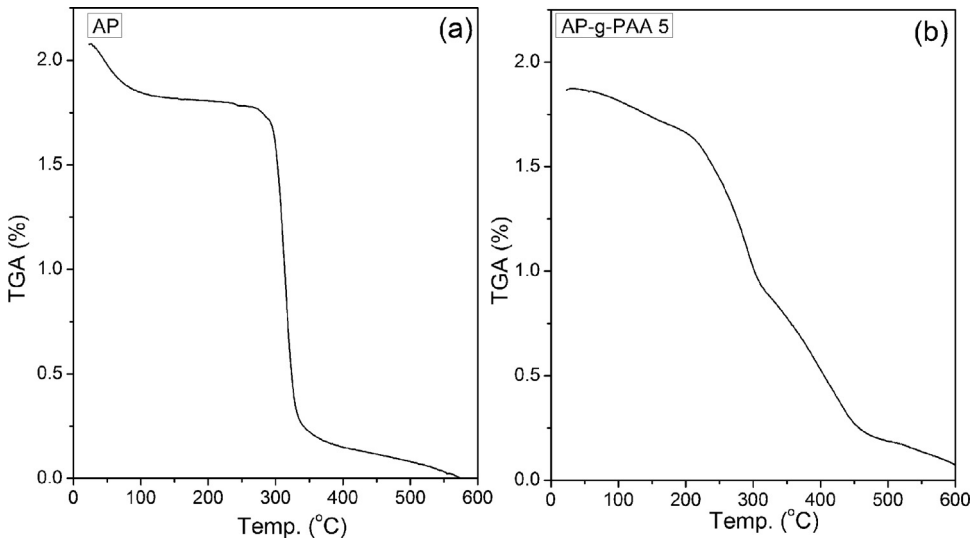

Fig. 3. Thermo gravimetric analysis of (a) AP and (b) AP-g-PAA 5.

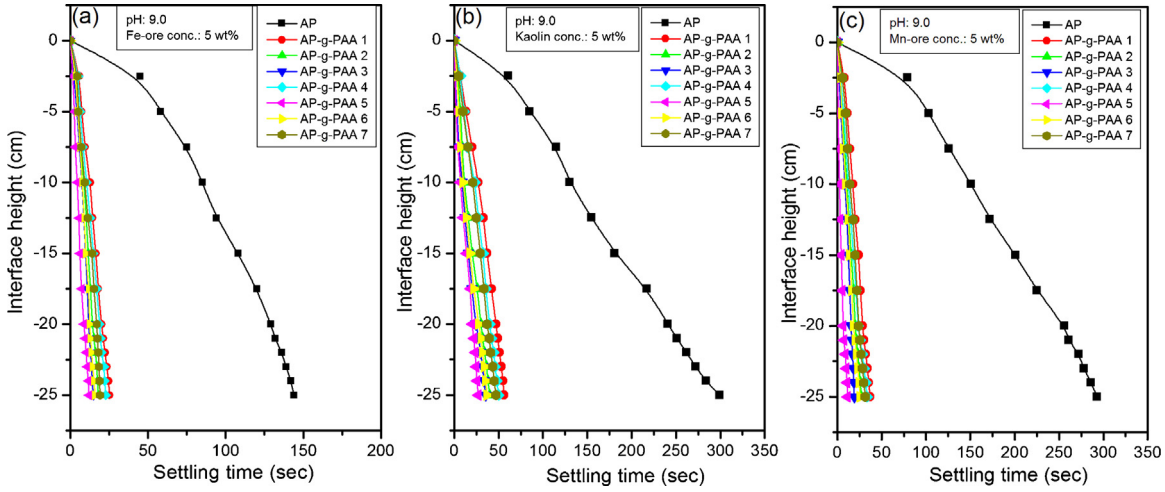

Fig. 4. Flocculation characteristics of (a) Fe-ore, (b) Kaolin, and (c) Mn-ore suspensions using AP and various graft copolymers as flocculants.

that the moiety grafted on a polysaccharide has more opportunity to form aggregates of the contaminants, since grafting enlarges the pervaded volume and thus increases the radius of gyration (Brostow et al., 2007) as well as hydrodynamic radius. It has also been observed that AP-g-PAA 5, which is having maximum % GE, intrinsic viscosity as well as higher hydrodynamic radius (Table 1), shows best flocculation efficiency. This is because of the fact that with increase in hydrodynamic radius as well as hydrodynamic volume (i.e. intrinsic viscosity), the approachability of the contaminants towards the modified polysaccharide enhanced and thereby increasing the flocculation efficacy (Brostow et al., 2007; Singh et al., 2000; Singh et al., 2003; Singh, 1995). From the settling curves, it is observed that the fall of interface is linear. The settling velocity is measured from the slope of the linear portion of the settling curves. The natural settling velocity of kaolin, Fe-ore and Mn-ore suspensions are 0.0641, 0.1344, 0.0657. From Fig. 4a–c, the settling velocities of the various suspensions with the addition of all the graft copolymers are calculated and the values are given in

Table 2
Average floc size and settling velocity of various suspensions using laboratory synthesized flocculants.

Polymeric flocculant	Average floc size (nm)			Settling velocity (cm/s)		
	Fe-ore suspension	Kaolin suspension	Mn-ore suspension	Fe-ore suspension	Kaolin suspension	Mn-ore suspension
Without flocculant	397.0	123.3	294.9	0.1344	0.0641	0.0657
Amylopectin	822.6	580.2	375.1	0.1736	0.0853	0.0836
AP-g-PAA 1	1348	1065	557.7	0.9893	0.6756	0.4464
AP-g-PAA 2	1854	2056	668.9	1.4037	0.9259	0.6250
AP-g-PAA 3	2655	2546	1189	1.6937	1.3157	0.7042
AP-g-PAA 4	1658	1204	401.1	1.0984	0.7462	0.5000
AP-g-PAA 5	**3204**	**2833**	**1467**	**2.0780**	**2.1968**	**0.9250**
AP-g-PAA 6	2571	2370	822.6	1.5812	0.9803	0.6756
AP-g-PAA 7	1809	1962	557.7	1.3150	0.7936	0.5319

Bold values indicates that AP-g-PAA 5 graft copolymer is the optimized one & showed best performance.

Table 3
Flocculating effect for treatment of mining industrial wastewater.

Flocculant	Turbidity (NTU)	TS (ppm)	TDS (ppm)	TSS (ppm)	COD (ppm)
Without flocculant	510	790	286	504	392
AP	210	492	162	330	272
AP-g-PAA1	91.7	390	245	145	182
AP-g-PAA2	81.1	292	190	102	131
AP-g-PAA3	72.4	240	164	76	119
AP-g-PAA4	86.2	357	235	122	155
AP-g-PAA5	64.7	190	135	55	108
AP-g-PAA6	78.5	266	179	87	126
AP-g-PAA7	84.6	330	221	109	138

Table 2. It is evident that the settling rate for various suspensions with addition of AP-g-PAA 5 is found to be maximum, which implies that AP-g-PAA 5 shows better flocculation characteristics than others. It is also apparent from Table 2 that flocs obtained from AP-g-PAA 5 were much larger in size for all the suspensions, in comparison with other flocculants, which corroborates that AP-g-PAA 5 is the best flocculant developed in this study.

The mechanisms of flocculation by grafted polysaccharide may be explained by either charge neutralization mechanism or polymer bridging mechanism. The charge neutralization occurs if the charge of the flocculant is opposite in sign to that of the suspended particles. The addition of such polymers to the suspension will result in an aggregation caused by specific ion adsorption (Singh et al., 2003). For neutral flocculants/slightly ionic flocculants, the major mechanism is the polymer bridging (Smalley, Hatharasinghe, Osborne, Swenson, & King, 2001; Zhou & Franks, 2006). In polymer bridging, the polymers having high molecular mass are adsorbed onto the particle surface and form bridges between adjacent particles. In the early experimental and theoretical investigations, La Mer and his group (LaMer & Healy, 1963) explained the bridging mechanism of flocculation using water soluble polymers as flocculants. For effective bridging to occur, the length of the polymer chains should be long so that they can expand from one particle surface to another (Nayak & Singh, 2001). So, the polymer with longer grafted chains would be more efficient as flocculant. This is the reason for better flocculation characteristics of AP-g-PAA 5.

3.4.2. Flocculation characteristics for mining industry wastewater treatment

It is well known that industrial wastewater constitutes an important part of the total wastewater from various sources. Reusage of industrial wastewater is based on settling out the solid constituents out of suspension. The treated wastewater may not be considered as potable, however it can be significant for possible agricultural and industrial reuse. Flocculation is an important phenomenon for purification of mining industry wastewater for its reuse, as it can decrease the total pollutant content from the wastewater. Table 3 represents the results of analysis for treatment of mining industry wastewater using various flocculants. It clearly demonstrates that AP-g-PAA 5 considerably reduce the overall pollutant load (i.e. Turbidity, TS, TDS, TSS, COD). Further, the colour profile (absorbance vs. wavelength) of supernatants drawn from the treated wastewater (Fig. 5) revealed impressive performance in removal of colour using various flocculants. However, here also AP-g-PAA 5 illustrates the maximum colour removal ability.

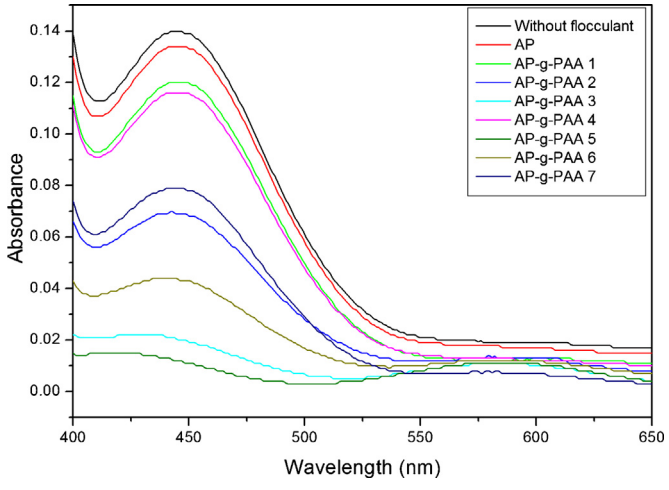

Fig. 5. Comparative study of efficiency of various flocculants in colour removal from mining industry wastewater.

4. Conclusion

From the above experimental observations, it can be concluded that by grafting PAA chains onto AP, it is possible to develop an efficient polymeric flocculant based on modified polysaccharide for the treatment of industrial wastewater. It has been observed that out of various graft copolymers, the graft copolymer which is having highest hydrodynamic radius as well as hydrodynamic volume is the best flocculant in compared to others.

Supplementary information available

Scheme for graft copolymer synthesis, effect of reaction parameters onto % GE, measurement of intrinsic viscosity, details of flocculation experiments, results of elemental analysis, rheological characteristics with rheological parameters results.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.03.025.

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